Effects of high pressure on the electric field gradient in *sp* metals

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The effect of high pressure on the electric field gradient (EFG) present at ^{111}Cd impurity nuclei in *sp* host metals of Zn, In, β-Sn, and Tl has been measured by the time-differential perturbed angular correlation technique. The pressure range was up to 40 kbar for Tl and up to 30 kbar for other hosts. The EFG decreases with pressure for Zn and Tl hosts and increases for Sn and In. In all hosts the rate of change of the EFG with volume $(\partial \ln q/\partial \ln V)_{c/a,T}$ is in agreement with systematics. The results are compared with calculations based on existing theoretical approaches.

I. INTRODUCTION

A considerable amount of data about electric field gradients (EFG) in noncubic metals is presently available and various general and important trends of systematical behavior of these fields have been established.[1–4] However, despite several successful specific theoretical studies, no theory exists that explains the observed behaviors in a comprehensive way. It seems that more experimental information is necessary. In particular, high-pressure studies are a powerful source of information about EFG, since pressure is the most pure method of changing the lattice parameters.

An interesting general property of the EFG emerged recently from pressure data studies by Butz and Kalvius.[5] They found that the volume dependence of the EFG *eq* in metals is very strong, namely,

$$\left(\frac{\partial \ln q}{\partial \ln V}\right)_{c/a,T} \approx -3 \ ;$$

whereas a value of -1 was expected for this rate if all the charges change in position isotropically under pressure, like the lattice contribution. This general behavior is not yet understood.

From the theoretical side, two successful approaches have been used to interpret the EFG pressure dependence in metals; Das and co-workers studied the EFG on Cd using a detailed band-structure calculation,[6] and Nishiyama and Riegel[7] investigated the fields on Cd and In in a semiempirical screening model. Despite the first attack being more rigorous and having no free parameters the simplicity and generality of the latter is attractive.

In this paper we present an experimental study of the effects of high pressure on the EFG acting on ^{111}Cd probe nuclei embedded in the *sp* metals Zn, β-Sn, In, and Tl. The measurements were made by means of the time-differential perturbed angular correlation (TDPAC) technique. The pressure range was up to 40 kbar for Tl and up to 30 kbar for the other hosts. We compare our results with a Hartree screening model in an approach similar to the one of Nishiyama and Riegel[7] and discuss the volume dependence obtained. A first account of the Zn and Sn experimental results has already been presented.[8]

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

A foil of silver was bombarded with α particles producing radioactive ^{111}In. After chemical separation the radioactive In was electroplated, together with minute amounts of In carrier, on small foils of the host metals of Zn, In, and Sn (purity 99.99). The foils were then sealed in evacuated quartz capsules and melted in a furnace. For the Zn host a distillation was performed producing small spheres of the metal. As Tl is a very oxidizable material, the electroplating of In was done first on a tungsten wire, which was then placed in an evacuated quartz tube, together with Tl, after which the same procedure as for Zn was used. The In contents in the hosts of Sn, Tl, and Zn was respectively 0.5, 0.1, and < 0.01 at.%.

B. TDPAC measurements

The ^{111}In nuclei decay by electron capture to ^{111}Cd, which is our probe nucleus. From the TDPAC measurement of the 173–247 keV γ cascade, knowing the electric quadrupole moment Q of the $\frac{5}{2}$ intermediate level in ^{111}Cd, we can extract the EFG *eq* acting on the probe nucleus. Following the usual procedure, we obtain the perturbation factor $G_{22}(t)$ from coin-

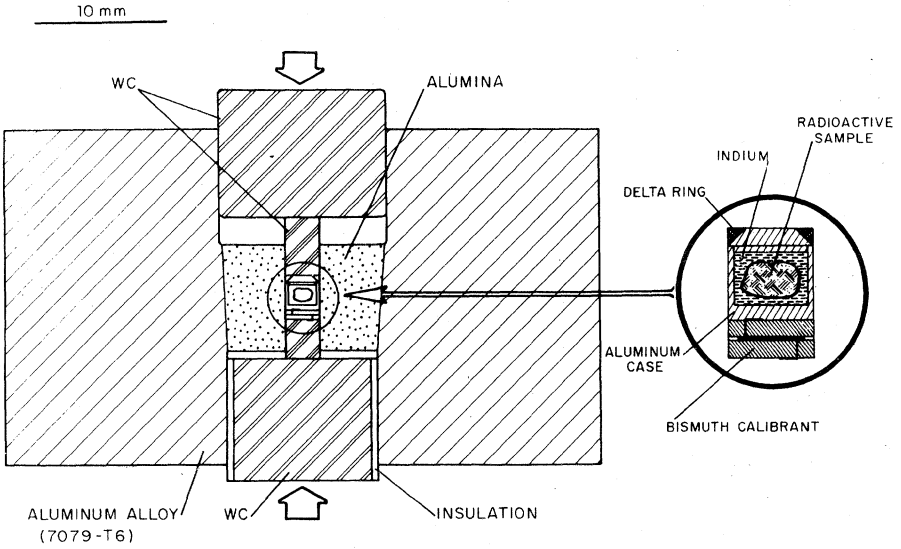

FIG. 1. Schematic diagram of the high-pressure chamber.

cidences recorded at angles of 90° and 180°, which is fitted with the theoretical expression for a polycrystalline sample given by[9]

$$G_{22}(t) = \sigma_{20} + \sum_{n=1}^{3} \sigma_{2n} \cos(\omega_n t) \ . \quad (1)$$

As the asymmetry parameter of the EFG was zero in all measurements, the frequencies ω_n have the simple relation $\omega_n = n\omega_1$ with

$$\omega_1 = \frac{3\pi}{10} \nu_Q \ ,$$

where $\nu_Q = e^2qQ/h$ is the nuclear quadrupole frequency.

D. High-pressure chamber

The high-pressure chamber was of the piston in cylinder type,[10] and is shown schematically in Fig. 1. It consists of a hard alumina cylinder shrink fitted to an outer support cylinder of hard aluminum alloy. Two tungsten carbide pistons slide inside the inner cylinder and compress the sample which is surrounded by metallic indium in an aluminum case. Together with the sample, a bismuth calibrant was installed to achieve good reliability in pressure calibration. The use of materials having light nuclei allows a tolerable absorption of the γ rays by the chamber walls. For the present γ cascade, the counting rate was about 40% of the one without the chamber.

In all the cases the measurements were done at room temperature.

TABLE I. Electric quadrupole frequencies on ^{111}Cd in the hosts of Zn, β-Sn, In, and Tl as function of pressure.

Pressure (kbar)	ν_Q (MHz)	Pressure (kbar)	ν_Q (MHz)
Zn		β-Sn	
0	133.5(7)	0	37.0(2)
10(1)	126.2(7)	10(1)	38.8(2)
20(1)	118.8(7)	20(1)	40.2(2)
30(1.5)	113.4(7)	30(1.5)	41.5(2)
In		Tl	
0	16.7(3)	0	8.0(4)
9(1)	18.5(3)	10(1)	7.3(4)
11(1)	18.8(3)	15(1)	6.8(5)
18(1.5)	20.1(3)	20(1)	7.0(4)
28^{+2}_{-1}	21.4(3)	25.4(5)	6.7(5)
		30(1)	6.6(4)
		35(1.5)	6.1(5)
		37(1.5)	66% − 0.0(10) 33% − 6.7(10)
		40(1.5)	0.0(4)

III. EXPERIMENTAL RESULTS

The experimental results for the various hosts and pressures are shown in Table I, where the quadrupolar interaction frequency ν_Q was extracted from the experimental $A_{22}G_{22}(t)$ curves by a least-square fitting to the theoretical expression (1).

Some of the $A_{22}G_{22}(t)$ experimental curves are displayed in Fig. 2. In all cases we observe a zero asymmetry parameter of the EFG and nearly no frequency distribution. Also in all the cases the zero-pressure quadrupole interaction frequency was the same before and after pressing, being always in good agreement with previous measurements by other authors.[11] The behavior of ν_Q under pressure for the systems studied here are shown graphically in Fig. 3 together with theoretical curves which are discussed in Sec. IV.

Based on the experimental data, we calculated the rates

$$\left(\frac{\partial \ln q}{\partial P}\right)_T \quad \text{and} \quad \left(\frac{\partial \ln q}{\partial \ln V}\right)_{c/a,T},$$

which are shown in Table II. The values for the first expression, giving the rate of change of ν_Q with pressure at constant temperature, were obtained from fitting the experimental points by a straight line. For In where nonlinear effects are more pronounced a polynomial of degree two in the pressure was used. The

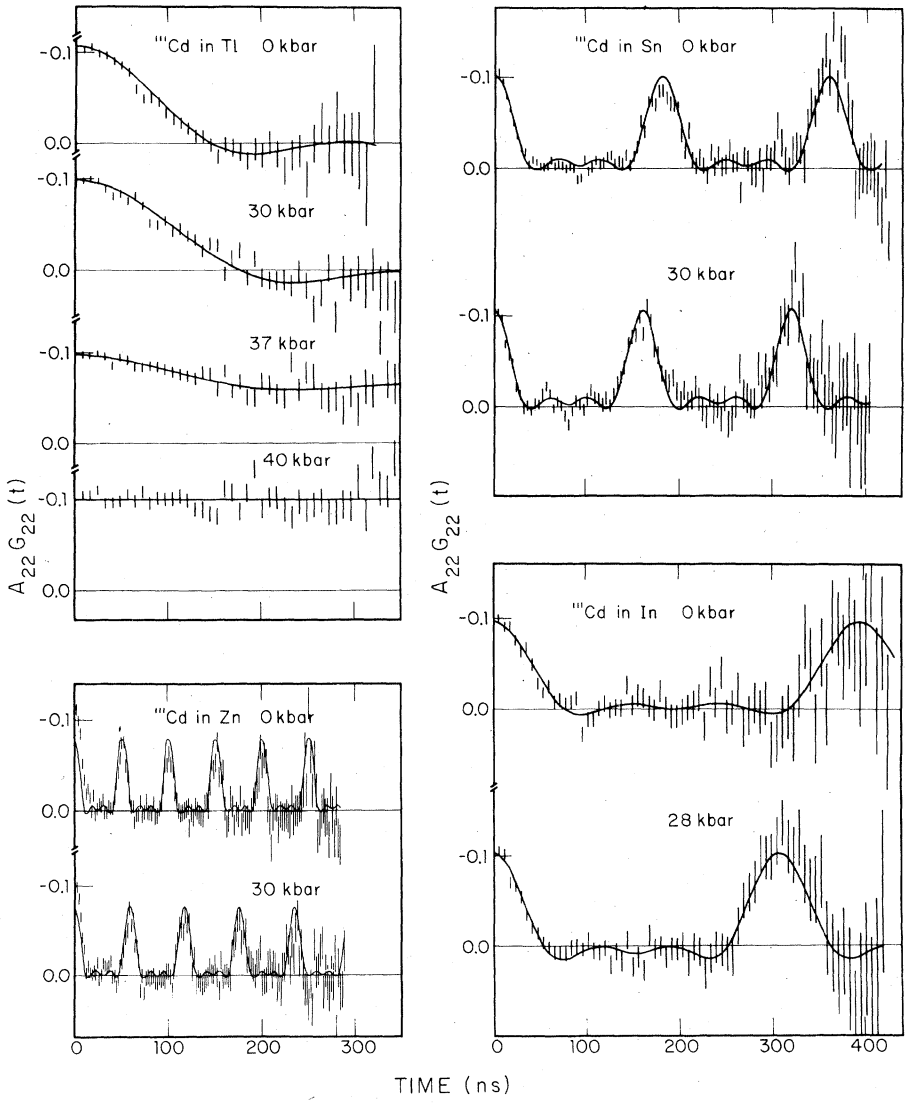

FIG. 2. $A_{22}G_{22}(t)$ perturbation factor of ^{111}Cd in the sp metals of Tl, β-Sn, Zn, and In for various pressures.

estimated values of the rate of change of q with volume were obtained by using the phenomenological expression involving the EFG eq as function of temperature, volume, and the c/a ratio,

$$\left(\frac{\partial \ln q}{\partial P}\right)_T = \left(\frac{\partial \ln q}{\partial \ln V}\right)_{c/a,T}\left(\frac{\partial \ln V}{\partial P}\right)_T + \left(\frac{\partial \ln q}{\partial \ln c/a}\right)_{V,T}\left(\frac{\partial \ln c/a}{\partial P}\right)_T . \quad (2)$$

The rate of change of q with the ratio c/a at constant volume is not known. This difficulty was overcome by using the prescription of Ref. 5 where for close-packed metals the following relation is assumed:

$$q \sim \left[\frac{c}{a} - \left(\frac{c}{a}\right)_0\right]$$

at constant volume and temperature. The ratios $(c/a)_0 = 1.633$ for hcp (Zn and Tl) and $(c/a)_0 = 1$ for tcp (In) structures were used. For the case of β-Sn, having a double tbc structure, there is no such prescription. However, the compressibility for tin is nearly isotropic and we can make a rough estimate

TABLE II. Rates of change of the EFG eq with pressure and with volume (see text).

Host	$\left(\frac{\partial \ln q}{\partial P}\right)_T$ (10^{-3} kbar^{-1})	$\left(\frac{\partial \ln q}{\partial \ln V}\right)_{c/a,T}$
Zn	−5.6(4)	−2.6(5)
β-Sn	4.1(3)	−2.5(10)
In	13.0(8)	−3.2(5)
Tl	−6(1.6)	−3.3(8)

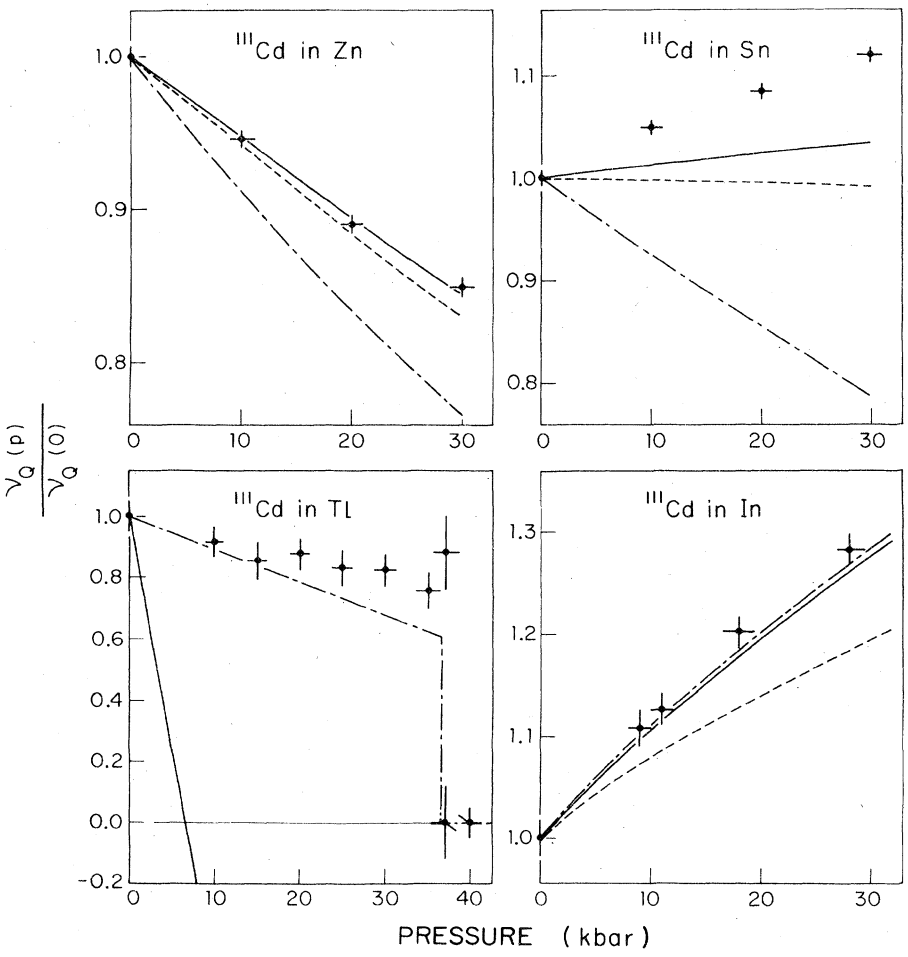

FIG. 3. Comparison of the pressure dependence of $\nu_Q(P)/\nu_Q(0)$ (+ experimental data) with theoretical predictions: (----) Hartree screened; (——) Hartree screened plus DWF; (—·—·—) Coulomb point charge.

neglecting the last term in Eq. (2). We then find for Sn

$$\left(\frac{\partial \ln q}{\partial \ln V}\right)_{c/a,T} = -2.5(10) ,$$

where the large quoted error considers an uncertainty in $(\partial \ln q/\partial \ln c/a)_{V,T}$ of ± 20.

The lattice parameters as function of high pressure and the compressibilities were taken from x-ray measurements for Zn,[12] In,[13] and Sn,[14] and from neutron-diffraction study in the case of Tl.[15] For In in the low-pressure region, the lattice parameters determined by x rays[13] are at variance with those measured by single-crystal deformation up to 3 kbar.[16] We used the latter more accurate values in dealing with the pressure derivatives in Eq. (2).

The quoted errors in Table II do not consider the uncertainty in the lattice parameter under pressure.

The pressure dependence of the lattice parameters for Zn used in our previous communication[8] differ from the data of Ref. 12 which are used in the present interpretation.

IV. DISCUSSION

The EFG, eq, felt by a probe nucleus can be expressed as[17]

$$eq = 2\int \frac{P_2(\cos\theta)}{r^3}\rho(\vec{r})[1-\gamma(r)]\,d\vec{\tau} , \qquad (3)$$

where $\rho(\vec{r})$ is the electric charge density, excluding the probe nucleus and core electrons, and $\gamma(r)$ is the Sternheimer factor that accounts for the EFG contribution from the polarization of the probe core electrons.

Usually the EFG in metals is analyzed as consisting of two separable contributions: the ionic, q_{latt}, generated by the ions other than the probe, and the conduction electron contribution, q_{el}, due to the conduction electrons, mainly those inside the probe Wigner-Seitz cell.[18] As $\gamma(r)$ is in general small inside the core radius and goes rapidly to the asymptotic value γ_∞ outside the core, the following approximate expression has traditionally been used:

$$q = q_{\text{latt}}(1-\gamma_\infty) + q_{\text{el}}(1-R) , \qquad (4)$$

where R is a small shielding constant that describes the core distortion due to charges inside the Wigner-Seitz cell, and is often neglected. We also neglect, in Eq. (4), the effect of the shielding due to conduction electrons outside the Wigner-Seitz cell, but that contribution, called distant, is not large for sp metals.[18] Another important shortcoming of Eq. (4) was recently pointed out by Das and co-workers,[19] who found for a sizeable part of q_{el} a very strong antishielding constant, roughly $\frac{1}{2}\gamma_\infty$, instead of R.

In spite of the easiness of calculating q_{latt} through a lattice sum, the computation of q_{el}, an often dominant term, is a very difficult task because it involves the evaluation of the true conduction electron wave functions by complicated band-structure calculations. So, considering the shortcomings of Eq. (4) and the difficulty of estimating its main contribution q_{el}, it seems that this equation is inadequate for analyzing pressure data. On the other hand, Raghavan *et al.*,[1] using Eq. (4), found a correlation between q_{el} and $q_{\text{latt}}(1-\gamma_\infty)$, proposing that

$$q_{\text{el}} \approx -Kq_{\text{latt}}(1-\gamma_\infty) . \qquad (5)$$

Here K is a "universal" constant whose value is about 3. This constant, or rather $-K(1-\gamma_\infty)$, seems to act as a kind of Sternheimer factor for the conduction electrons inside the probe atom. In this view q_{el} would be induced by q_{latt}. If this is the case we would expect an increase of K with the increase in conduction-electron density. In Fig. 3 we show a comparison between the experimental points of the EFG normalized to zero pressure and the calculated q_{latt} (dash-dotted curve) assuming a Coulomb field, generated by the ions plus a uniform compensating background. As we can see, the experimental points always lie above the q_{latt} curve, indicating that if we consider γ_∞ as pressure independent, K increases with increasing pressure. This behavior is also present in other systems such as ^{111}Cd *Cd*. So it seems that in fact K increases with the conduction electron concentration and the increase of K is much stronger in Sn than in the other hosts. It is also interesting to note that Lis and Naumann,[20] studying the EFG in Hume-Rothery alloys, found an increase of the EFG with the electron/atom ratio, although in this case there could be an extra complication due to severe Fermi-surface distortions.

Most of the experimental data follow relation (5), which was found empirically. Although efforts have been made to understand it, none of them have succeeded in explaining the magnitude of K.[21]

Another important approach to treat the EFG in metals was initially undertaken by Sholl[22] and was extensively used by Nishiyama and Riegel[7] to explain temperature and pressure experiments. In this approach the effect of conduction electrons is incorporated by calculating the EFG generated by the lattice ions with a Coulomb potential shielded by the conduction electrons through linear Hartree screening. The electric potential is then

$$V(r) = \frac{1}{2\pi^2}\int_0^\infty \frac{V(k)}{\epsilon(k)}\frac{\sin(kr)k^2\,dk}{kr} , \qquad (6)$$

where $V(k)$ is the Fourier transform of the bare Coulomb potential of an ion and $\epsilon(k)$ is the static Hartree dielectric function given by

$$\epsilon(k) = 1 + \frac{1}{2\pi a_H k_F \eta^2}\left(\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| + 1\right) ,$$

where k_F is the free-electron Fermi wave vector,

$$\eta = \frac{k}{2k_F} \quad \text{and} \quad a_H = \frac{\hbar^2}{me^2} .$$

The EFG derived from the potential given by Eq. (6) is then summed over the lattice of ions to give the screened EFG eq_{sc}. In the work of Nishiyama and Riegel a free parameter, the enhancement factor A, is used to take account of the atomiclike character of the conduction electrons near the probe and an additional Debye-Waller factor (DWF) also arises due to the thermal vibration of the ions. This factor is weakly dependent on pressure. The EFG is then written

$$q = q_{sc} A (1 - \gamma_\infty) \exp[-\tfrac{4}{3} \langle (\Delta x)^2 \rangle k_F^2] .$$

Despite the strong doubts about the validity of this equation, the authors of Ref. 7 find good agreement in explaining temperature and pressure experiments in some *sp* metals.[3,7] We made calculations of q_{sc} as a function of pressure for all the present cases by means of a numerical integration. The results of these calculations normalized to zero pressure, are shown as dotted lines in Fig. 3. The full curves represent the inclusion in the calculation of the DWF. The agreement is not good in all the cases, and for Tl, the screened term gives a very bad description of the observed behavior. We think that the failure of this model is not surprising if we consider its various shortcomings. Apart from some serious questions regarding the validity of the Coulomb potential in metals and the associated use of linear screening theory it must be remembered that this screening model does not consider the strong variation in the Sternheimer factor $\gamma(r)$ near the core radius.[3] However, the excellent agreement in the case of Zn is very striking.

In the following, some aspects peculiar to each of the hosts are discussed separately.

A. Zn host

In this case we can see from Fig. 3 that the measured EFG decreases more slowly than that predicted from a point-charge model. The Hartree screened potential gives a good agreement, and the inclusion of the DWF turns out to be in excellent agreement with the experimental results. We note that the behavior of the EFG on ^{111}Cd in Zn under pressure is similar to the one observed by Raghavan *et al.*[23] for ^{111}Cd in Cd. This is expected due to the close similarities between these two metals (Zn and Cd), having the same valence, a very high c/a ratio, and highly anisotropic compressibilities.

B. In host

Our result for pressures up to 28 kbar, showing a large increase of the EFG, is in agreement with previous measurements in the range up to 8 kbar using probe nuclei of ^{115}In[16] (in a NMR experiment) and ^{111}Cd[24] (in a TDPAC experiment) in the same host. This fact is important, since it suggests that for In host the behavior of the EFG under pressure is independent of the probe atom.

From Fig. 3 we can see that the Coulomb point-charge model calculation follows closely the observed results, but the experimental points still lie above this curve. The Hartree screened potential EFG gives a worse result. However, the inclusion of the DWF gives a satisfactory description of the experimental points. Our calculations agree with those already done by Nishiyama and Riegel,[7] except for q_{latt}, where these authors used too small a number of points in their lattice summation.[25]

C. β-Sn host

For tin host we found a clear increase of the EFG with pressure, whereas the Coulomb point charge plus uniform background model predicts a strong decrease, as is shown in Fig. 3. Also, the Hartree shielding model without and with the DWF does not reproduce the data, giving too small an EFG change under pressure. The large departure of the point-charge model from the experimental results is remarkable, because in other cases this disagreement is not so dramatic. What we observe here seems to be a proof of the independence of q_{el} from q_{latt} in Sn, as was anticipated by Collins and Benczer-Koller.[26] These authors noted that if the correlation between q_{el} and q_{latt} arises only from the same structural dependence of those two quantities, then far away from a c/a ratio where the EFG must vanish by symmetry arguments, q_{el} would be independent of q_{latt}. This is especially true for Sn, where the c/a value of 0.546 is close to an "accidental" vanishing of the point charge EFG at 0.540 07, whereas the symmetry zero is for $c/a = 1.414$.

D. Tl host

In this case the quadrupolar interaction frequency is very low and as can be seen in Fig. 2 we have observed less than half a period. So, some doubts could exist about the precise location of all the probe nuclei and a consequent frequency distribution could occur, instead of a unique interaction frequency. However, as can be seen from Fig. 2 at about 37 kbar we reach the hcp-fcc phase transition of Tl,[15] where the frequency becomes zero, as it is expected from a uniform substitutional location of the ^{111}Cd probes.

From Fig. 3 we can see that again the point-charge EFG lies below the experimental points. Here the Hartree screened EFG (with or without the DWF) gives a completely wrong trend, changing sign at about 7 kbar. It could be argued that this severe failure of the screening model is due to local distortion, arising from size mismatch between ^{111}Cd and Tl. However the metallic radii of Cd and Tl are not so different and the addition of Cd to Tl gives relatively small lattice parameters changes.

The estimated volume dependence of the EFG in Tl host is also in close agreement with the systematic trend, namely,

$$\left(\frac{\partial \ln q}{\partial \ln V}\right)_{c/a,T} = -3.3(8) \ .$$

IV. CONCLUSIONS

From the above results and discussions we see that all our results agree with the systematics found by Butz and Kalvius, showing a high volume dependence for the EFG in metals (see Table II). This general behavior is remarkable, and demands a theoretical effort to be explained, although a tentative approach has already been made.[27]

The analysis of our data using an EFG derived from a Hartree screened Coulomb potential, following Nishiyama and Riegel,[7] resulted in good agreement in two cases only (Zn and In) and gave in fact a very bad description in the case of Tl.

We do not expect that the obtained results are strongly affected by the impurity problem we are dealing with, because ^{111}Cd is also an *sp* impurity and produces a relatively small local distortion in the studied hosts. Moreover the linear screening theory we are using is independent of the kind of probe, except by a different DWF, but this factor is not strongly pressure dependent. In this respect it is interesting to remark that the EFG pressure dependence of ^{111}Cd in In is the same as for ^{115}In in In.

From the fact that the experimental EFG points always lie above the predicted curve based on the point charge plus uniform background model, we conclude that the correlation constant K of Eq. (4) always increases with pressure, and for β-Sn this increase is unusually large, overcompensating the large decrease in q_{latt}. This strange behavior of tin is in clear accordance with the considerations of Collins and Benczer-Koller[26] who suggested an independence of q_{el} from q_{latt} in tin, based on the large departure of β-Sn lattice from the point where the EFG must vanish by symmetry. This is also in agreement with the suggestion of Butz[4] that the correlation represented by Eq. (4) follows from a similar structure dependence of q_{el} and q_{latt}, instead of q_{el} being induced by q_{latt}.

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